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(54) EASILY BONDABLE SYNDIOTACTIC POLYSTYRENE-BASED BIAXIALLY ORIENTED FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To improve the transparency and adhesion of a film by a method wherein as a specified self-crosslinkable polyester-based graft copolymer, which includes one kind of a monomer containing an anhydride having a double bond, is formed on one side of a syndiotactic polystyrene-based biaxially oriented film.

SOLUTION: On one side of a syndiotactic polystyrene-based biaxially oriented film, in which either one of lubricants such as inert particles or the like is singly used for a syndiotactic polystyrene-based polymer consisting of particles made of a metal oxide such as silica, titanium dioxide, talc, kaolinite or the like; a metal salt such as calcium carbonate, calcium phosphate, barium sulfate or the like of an organic polymer; a self-crosslinkable polyester-based graft copolymer, in which one kind or more of polymerizable unsaturated monomers is grafted to a hydrophobic polyester-based resin. The graft copolymer contains one kind of monomer including an anhydride having a double bond.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a syndiotactic polystyrene system biaxially oriented film and the easy adhesiveness syndiotactic polystyrene system biaxially oriented film which was excellent in transparency and an adhesive property when saying in more detail.

[0002]

[Description of the Prior Art] A syndiotactic polystyrene system biaxially oriented film is excellent in thermal resistance, an electrical property, transparency, etc., and expansion is expected from various kinds of film applications, such as an object for magnetic tapes, a photograph and the object for platemaking, an object for capacitors, and an object for a package. When using a film as wrapping especially, the need is accepted at least at one side of the film by which biaxial stretching was generally carried out. Printing and an organic barrier layer, After giving inorganic or a metal vacuum evaporations layer and forming adhesives further, [whether a sealant layer is prepared by the dry laminate method, and] Or prepare a sealant layer by the extrusion laminating method, consider as the layered product of a film, create a bag using this layered product, and opening after restoration is heat sealed for contents. For example, moisture content food or chemicals, such as seasonings, such as bean paste and soy sauce, soup, and a pouch-packed food, etc. are packed, and it provides for a consuming public. Moreover, in case the above-mentioned layered product is constituted from the former, in consideration of the adhesive property with a printing layer, an organic barrier layer or a sealant layer, etc., it is made general to prepare an adhesion reforming layer.

[0003]

[Problem(s) to be Solved by the Invention] However, in the case of the above-mentioned polystyrene system film, it is difficult for the property to prepare a reason and an adhesion reforming layer. For example, if the conventional drainage system paint is used, since the surface energy of this film is low, HAJIKI of coating liquid will arise, and an appearance will be spoiled. Moreover, it is not desirable when the paint of a solvent system is used, and health nature and recycle nature are taken into consideration. Then, this invention aims at offering the laminating syndiotactic polystyrene system biaxially oriented film excellent in the adhesive property with a sealant layer by applying the drainage system paint which can be applied to the above-mentioned polystyrene system film, and this drainage system paint.

[0004]

[Means for Solving the Problem] The above-mentioned purpose can be attained by forming the syndiotactic polystyrene system film with which the laminating of the adhesion reforming layer to which it is the self-cross-linking polyester system graft copolymer with which the graft of one or more sorts of polymerization nature partial saturation monomers was carried out to hydrophobic polyester system resin, and said graft copolymer is characterized by including at least one sort of monomers containing the acid anhydride which has a double bond was carried out to at least one side of the syndiotactic polystyrene system biaxially oriented film of this invention. In the still more desirable

embodiment of this invention, it is that said polymerization nature partial saturation monomer contains the anhydride of a maleic acid, and the combination of styrene at least.

[0005] As a polystyrene system polymer whose stereoregularity used for this invention is syndiotactic structure polystyrene, Pori (p-, m-, or o-methyl styrene), and Pori (2 and 4-) Pori, such as 2, 5, -, 3, and 4- or 3, 5-dimethyl styrene, and Pori (p-tertiary butyl styrene) (alkyl styrene), Pori (p-, m-, or o-chloro styrene), Pori (p-, m-, or o-bromostyrene), Pori, such as Pori (p-, m-, or o-fluoro styrene) and Pori (o-methyl-p- fluoro styrene) (halogenation styrene), Pori, such as Pori (p-, m-, or o-chloromethyl styrene) (halogenation alkyl styrene), Pori, such as Pori (p-, m-, or o-methoxy styrene) and Pori (p-, m-, or o-ethoxy styrene) (alkoxy styrene), Pori, such as Pori (carboxy alkyl styrene) Pori (p-vinylbenzyl propyl), such as Pori (p-, m-, or o-carboxy methyl styrene), (alkyl ether styrene), Pori (alkyl silyl styrene), such as Pori (p-trimethylsilyl styrene), -- Pori (phospha[vinylbenzyl dimethoxy] id) etc. is mentioned further.

[0006] Especially in this invention, polystyrene is suitable in said polystyrene system polymer. Moreover, the polystyrene system polymer which has the syndiotactic structure of using by this invention does not necessarily need to be a single compound, and as long as syndiotacticity is said within the limits, mixture, and copolymers and those mixture with the polystyrene system polymer of atactic structure or isotactic structure are sufficient as it. Moreover, the weight average molecular weight of the polystyrene system polymer used for this invention is 50,000 or more still more preferably 10,000 or more. Weight average molecular weight cannot obtain the biaxially oriented film excellent in a strong ductility property or thermal resistance in less than 10,000 thing. Although not limited especially about the upper limit of weight average molecular weight, since generating of the fracture accompanying the increment in extension tension etc. arises, it is not so desirable at 1500 or 000 or more.

[0007] Furthermore, the syndiotactic polystyrene system biaxially oriented film of this invention is chosen according to many properties, such as reinforcement, dimensional stability, etc. which perform a well-known approach, for example, vertical extension, and horizontal extension in order and which can adopt the extension approaches, such as width, length and the length [besides the biaxial-stretching approach] extending method, length, width and the vertical extending method, and length, length, the horizontal extending method, serially, and are demanded. Moreover, it is required to perform heat setting processing, vertical relaxation processing, horizontal relaxation processing, etc. Moreover, any one sort may be independently used for lubricant, such as an inactive particle, to syndiotactic polystyrene system polymers, such as a particle which consists of a metaled salt or metaled organic polymers, such as metallic oxides, such as a silica, a titanium dioxide, talc, and a kaolinite, a calcium carbonate, calcium phosphate, and a barium sulfate, and two or more sorts may be used together.

[0008] (Graft polymer) Generally the graft polymerization of this invention is carried out in the condition of having dissolved hydrophobic copolymerized polyester resin into the organic solvent, by making a radical initiator and radical polymerization nature monomer mixture react. Although the resultant after graft-ized reaction termination also contains the radical polymerization object which was not graft-ized to the hydrophobic copolymerized polyester and hydrophobic copolymerized polyester which did not receive graft-ization other than the graft polymer between desired hydrophobic copolymerized polyester-radical polymerization nature monomer mixture, these [all] are contained with the graft polymer in this invention.

[0009] As for the acid number of the reactant which carried out the graft polymerization of the radical polymerization nature monomer to hydrophobic copolymerized polyester resin, in this invention, it is desirable that they are more than 600eq(s)/106 g. The acid numbers of a reactant are more than 1200eq (s)/106 g more preferably. When the acid numbers of a reactant are under 600eq(s)/106 g, an adhesive property with the layer covered by the priming material which is the purpose of this invention cannot say that it is enough.

[0010] moreover, the desirable weight ratio of hydrophobic copolymerized polyester resin and a radical polymerization nature monomer which suits the purpose of this invention -- the range of polyester / radical polymerization nature monomer = 40 / 60 - 95/5 -- desirable -- further -- desirable -- 55 / 45 - 93/7 -- it is the range of 60 / 40 - 90/10 most desirably. When the weight ratio of hydrophobic

copolymerized polyester resin is less than 40 % of the weight, the adhesive property which was excellent in polyester resin cannot be demonstrated. On the other hand, when the weight ratio of hydrophobic copolymerized polyester resin is larger than 95 % of the weight, the blocking which is the fault of polyester resin becomes easy to take place.

[0011] The graft polymerization reactant of this invention becomes the gestalt of the solution of an organic solvent, dispersion liquid, the solution of a drainage system solvent, or dispersion liquid. Especially, the dispersion liquid of a drainage system solvent, i.e., the gestalt of moisture powder resin, are desirable in respect of work environment and spreading nature. In order to obtain such moisture powder resin, in an organic solvent, the graft polymerization of the radical polymerization nature monomer which contains a hydrophilic radical polymerization nature monomer in said hydrophobic copolymerized polyester resin is carried out, and, subsequently it is usually attained by water addition and organic solvent distilling off. The average particle system by which the moisture powder resin in this invention is measured with laser light scattering measurement is 500nm or less, and presents the appearance of translucence thru/or opalescence. Although the moisture powder resin of various particle diameter is obtained by adjustment of a polymerization method, 10-500nm is suitable for this particle diameter, and it is the point of distributed stability, and 400nm or less is desirable and is 300nm or less more preferably. Since the fall of the gloss of a covering film front face will be seen, the transparency of a coating will fall and the water resisting property which is the purpose of this invention will fall in less than 10nm if 500nm is exceeded, it is not desirable.

[0012] The hydrophilic radical polymerization nature monomer used for the polymerization of the moisture powder resin in this invention points out the radical which has a hydrophilic group or can change to a hydrophilic group later. The radical polymerization nature monomer which contains a carboxyl group, a hydroxyl group, a phosphoric-acid radical, a phosphorous acid radical, a sulfonic group, an amide group, a quarternary-ammonium-salt radical, etc. as a radical polymerization nature monomer which has a hydrophilic group can be mentioned. On the other hand, an acid-anhydride radical, a glycidyl group, the Krol radical, etc. can be mentioned as a radical polymerization nature monomer which can change to a hydrophilic group. The radical polymerization nature monomer which has in these the radical which a carboxyl group is desirable, and has a carboxyl group, or generates a carboxyl group from a water-dispersion point is desirable. It is more desirable to contain the radical polymerization nature monomer which contains the carboxyl group or generates a carboxyl group at the point which raises the acid number of this invention.

[0013] (Polyester) It is necessary to distribute or dissolve and to twist hydrophobic copolymerized polyester resin in water, by itself, essentially, and it essentially needs to be [it is necessary to set to this invention, and] water-insoluble nature. If the polyester resin which distributes or dissolves in water is used for graft polymerization, the adhesive property and water resisting property which are the purpose of this invention will worsen.

[0014] As for the presentation of the dicarboxylic acid component of this hydrophobic copolymerized polyester resin, it is desirable that it is [0.5-10 mol] % of dicarboxylic acid containing the 60-99.5 mol % and aliphatic series dicarboxylic acid of aromatic series dicarboxylic acid and/or the 0-40 mol % and polymerization nature partial saturation double bond of alicycle group dicarboxylic acid. When the case where aromatic series dicarboxylic acid is less than [60 mol %], aliphatic series dicarboxylic acid, and/or alicycle group dicarboxylic acid exceed 40-mol %, bond strength falls.

[0015] Moreover, when efficient graft-ization of the radical polymerization nature monomer to polyester resin becomes is hard to be performed when the dicarboxylic acid containing a polymerization nature partial saturation double bond is less than [0.5 mol %] and it exceeds ten-mol % conversely, since viscosity rises also to remainder at the anaphase of a graft-ized reaction and a uniform advance of a reaction is barred, it is not desirable. Aromatic series dicarboxylic acid is 2-7 mol % containing 70-98-mol % and aliphatic series dicarboxylic acid and/or the 0-30 mol % and polymerization nature partial saturation double bond of alicycle group dicarboxylic acid of dicarboxylic acid more preferably.

[0016] As an example of aromatic series dicarboxylic acid, a terephthalic acid, isophthalic acid, an orthochromatic phthalic acid, naphthalene dicarboxylic acid, biphenyl dicarboxylic acid, etc. can be

mentioned. It is more desirable not to use hydrophilic-group content dicarboxylic acid, such as 5-sodium sulfoisophtharate, in that the water resisting property which is the purpose of this invention falls. As aliphatic series dicarboxylic acid, a succinic acid, an adipic acid, an azelaic acid, a sebacic acid, a dodecane dione acid, dimer acid, etc. can be mentioned, and 1, 4-cyclohexane dicarboxylic acid, 1, 3-cyclohexane dicarboxylic acid, 1, and 2-cyclohexane dicarboxylic acid, its acid anhydride, etc. can be mentioned as alicycle group dicarboxylic acid.

[0017] As an example of the dicarboxylic acid containing a polymerization nature partial saturation double bond, 2, 5-norbornene dicarboxylic acid anhydride, tetrahydro phthalic anhydride, etc. can be mentioned as alpha and beta-partial saturation dicarboxylic acid as a fumaric acid, a maleic acid, a maleic anhydride, an itaconic acid, a citraconic acid, and alicycle group dicarboxylic acid containing a partial saturation double bond. Among these, fumaric-acid [from the point of polymerization nature], maleic-acid, 2, and 5-norbornene dicarboxylic acid is desirable.

[0018] On the other hand, although a glycol component consists of the aliphatic series glycol of carbon numbers 2-10, an alicycle group glycol of carbon numbers 6-12, and/or an ether linkage content glycol As an aliphatic series glycol of carbon numbers 2-10 Ethylene glycol, 1, 2-propylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, neopentyl glycol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, 1, 9-nonane diol, a 2-ethyl-2-butyl propanediol, etc. can be mentioned, and 1 and 4-cyclohexane dimethanol etc. can be mentioned as an alicycle group glycol of carbon numbers 6-12.

[0019] As an ether linkage content glycol, a diethylene-glycol, triethylene glycol, dipropylene glycol, glycols [that add ethyleneoxide or propylene oxide to two phenolic hydroxyl groups of bisphenols further, and are obtained], 2 [for example,], and 2-bis(4-hydroxy ethoxy phenyl) propane etc. can be mentioned. A polyethylene glycol, a polypropylene glycol, and a polytetramethylene glycol can also be used as occasion demands.

[0020] Although % of 0-5-mol the polycarboxylic acid of three or more organic functions and/or, and polyol can be copolymerized in the copolymerized polyester resin used by this invention, as polycarboxylic acid of three or more organic functions, trimellitic acid (anhydrous), pyromellitic acid (anhydrous), benzophenone (anhydrous) tetracarboxylic acid, trimesic acid, ethyleneglycol bis (anhydrotrimellitate), glycerol tris (anhydrotrimellitate), etc. are used. On the other hand, a glycerol, trimethylolethane, trimethylol propane, pentaerythritol, etc. are used as polyol of three or more organic functions. the polycarboxylic acid and/or polyol of three or more organic functions -- all acid components or all glycol components -- receiving -- 0-5-mol % -- although copolymerization is desirably carried out in [0-3 mol] %, if five-mol % is exceeded, the gelation at the time of a polymerization tends to take place, and it is not desirable.

[0021] Moreover, the molecular weight of hydrophobic copolymerized polyester resin is 5000-50000 at a weighted mean. The range is desirable. If there is a fall of bond strength and 50000 is conversely exceeded when molecular weight is less than 5000, problems, such as gelation at the time of a polymerization, will occur.

[0022] (Polymerization nature partial saturation monomer content polymer) If the polymerization nature partial saturation monomer of this invention is illustrated, again Monoester, or the diester maleic acid and its anhydride of fumaric acids, such as a fumaric acid, fumaric-acid monoethyl, diethyl fumarate, and fumaric-acid dibutyl, Monoester or diester of a maleic acid, such as maleic-acid monoethyl, a diethyl maleate, and dibutyl maleate, Monoester or diester of an itaconic acid, and the anhydride and an itaconic acid, Maleimide, such as phenyl maleimide, etc. is styrene derivatives, such as styrene, alpha methyl styrene, t-butyl styrene, and chloromethyl styrene, vinyltoluene, a divinylbenzene, etc. again. moreover, an acrylic polymerization nature monomer -- for example, alkyl acrylate and alkyl methacrylate (as an alkyl group -- a methyl group --) An ethyl group, n-propyl group, an isopropyl group, n-butyl, an isobutyl radical, t-butyl, a 2-ethylhexyl radical, a cyclohexyl radical, a phenyl group, Benzyl, a phenylethyl radical, etc. : 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, The hydroxy content acrylic monomer of 2-hydroxypropyl methacrylate : Acrylamide, Methacrylamide, N-methyl methacrylamide, N-methylacrylamide, N-methylol acrylamide, N-methylolmethacrylamide, N and N-dimethylol acrylamide, N-methoxymethyl acrylamide, Amide

group content acrylic monomer: N of N-methoxymethyl methacrylamide and N-phenyl acrylamide, N-diethylamino ethyl acrylate, The amino-group content acrylic monomer of N and N-diethylamino ethyl methacrylate : Glycidyl acrylate, The epoxy-group content acrylic monomer of glycidyl methacrylate: The acrylic monomer containing carboxyl groups, such as an acrylic acid, methacrylic acids, and those salts (sodium salt, potassium salt, ammonium salt), or the salt of those is mentioned. Preferably, they are a maleic-acid anhydride and its ester. Copolymerization of the above-mentioned monomer can be carried out using one sort or two sorts or more.

[0023] Generally the graft polymerization of this invention is carried out in the condition of having dissolved hydrophobic copolymerized polyester resin into the organic solvent, by making a radical initiator and radical polymerization nature monomer mixture react. Although the resultant after graft-ized reaction termination also contains the radical polymerization object which was not graft-ized to the hydrophobic copolymerized polyester and hydrophobic copolymerized polyester which did not receive graft-ization other than the graft polymer between desired hydrophobic copolymerized polyester-radical polymerization nature monomer mixture, these [all] are contained with the graft polymer in this invention.

[0024] (Polymerization initiator and in addition to this additive) As a graft polymerization initiator which can be used by this invention, well-known organic peroxide and organic azo compounds can be used for this contractor. As organic peroxide, - azobisisobutyronitril, and 2 and 2 '2, 2'-azobis (2, 4-dimethyl PARERO nitril) etc. can be mentioned as benzoyl peroxide, t-butylperoxy perpivalate, and an organic azo compound. The amount of the polymerization initiator used for performing graft polymerization is 0.5 % of the weight or more preferably at least 0.2% of the weight or more to a polymerization nature monomer. The chain transfer agent for adjusting the chain length of a branch polymer other than a polymerization initiator, for example, an octyl mercaptan, mercaptoethanol, 3-t-butyl-4-hydroxyanisole, etc. can be used if needed. In this case, it is desirable to be added in 0 - 5% of the weight of the range to a polymerization nature monomer.

[0025] (Reaction solvent) As for the graft-ized reaction solvent for operation of this invention, it is desirable to consist of aquosity organic solvents whose boiling points are 50-250 degrees C: An aquosity organic solvent means that at least 10 or more g/L of whose solubility over the water in 20 degrees C is 20 or more g/L desirably here. Since that to which the boiling point exceeds 250 degrees C has a slow vapor rate to remainder and cannot fully be removed by elevated-temperature printing of a paint film to it, it is unsuitable. Moreover, when the boiling point carries out a graft-ized reaction by making it into a solvent below 50 degrees C, the initiator which **** to a radical at the temperature of 50 degrees C or less must be used, the risk on handling increases, and it is not desirable. As an aquosity organic solvent of the first group which dissolves comparatively well the polymerization nature monomer mixture which dissolves copolymerized polyester resin well and contains a carboxyl group content polymerization nature monomer, and its polymer Ester, for example, ethyl acetate, and ketones, for example, a methyl ethyl ketone, Methyl isobutyl ketone, a cyclohexanone, and cyclic ether, for example, a tetrahydrofuran, Dioxane, 1, 3-dioxolane, and glycol ether, for example, ethylene glycol wood ether, Propylene glycol methyl ether, propylene glycol pro PIRUE-Tell, Ethylene glycol ethyl ether, ethylene glycol butyl ether, Carbitols, for example, methyl carbitol, ethyl carbitol, butyl carbitol, Glycols or the low-grade ester of glycol ether, for example, ethylene glycol diacetate, Ethylene glycol ethyl ether acetate, ketone alcohol, for example, diacetone alcohol, and also N-permutation amides, for example, dimethylformamide, dimethylacetamide, N-methyl pyrrolidone, etc. can be illustrated.

[0026] On the other hand, as an aquosity organic solvent of the second group which dissolves comparatively well the polymerization nature monomer mixture which contains a carboxyl group content polymerization nature monomer although copolymerized polyester resin is hardly dissolved, and its polymer, although water, lower alcohol, low-grade carboxylic acids, low-grade amines, etc. can be mentioned, as a thing especially desirable to operation of this invention, it is the alcohols and the glycols of carbon numbers 1-4.

[0027] When a single solvent performs a graft-ized reaction, it can carry out by merely choosing a kind from the aquosity organic solvent of the first group. When a mixed solvent performs, a kind may be

chosen from the case where two or more sorts are chosen only from the aqueous organic solvent of the first group, and the aqueous organic solvent of the first group, at least, and a kind may be added to it at least from the aqueous organic solvent of the second group.

[0028] A graft polymerization reaction can be performed also in any the case where a graft polymerization reaction solvent is used as the single solvent from the aqueous organic solvent of the first group, and at the time of considering as the mixed solvent of the aqueous organic solvent of the first group and the second group which consists of a kind, respectively. However, it is more desirable for a difference to be seen by the appearance of the water dispersing element drawn from the advance behavior of a graft-ized reaction, a graft-ized resultant, and it, description, etc., and to use the mixed solvent of the aqueous organic solvent of the first group and the second group which consists of a kind, respectively.

[0029] In the solvent of the first group, it was checked by the measurement of viscosity of the copolymerized polyester in these solutions that a copolymerized polyester chain is in the condition that the large chain of breadth was extended, and it is in the condition of having twined in the shape of [of breadth / small] a yarn ball in the mixed solvent of the first group / the second group, on the other hand. It is effective in gelation prevention to make it hard to adjust the dissolution condition of copolymerized polyester and to happen intermolecular bridge formation. Coexistence of graft-izing with high effectiveness and gelation control is attained in the latter mixed solvent system. the weight ratio of the mixed solvent of the 1st group / the 2nd group -- more -- desirable -- 95 / 5 - 10/90 -- further -- desirable -- 90 / 10 - 20/80 -- it is the range of 85 / 15 - 30/70 most desirably. The optimal mixed ratio is determined according to the solubility of the polyester to be used etc.

[0030] (Formation of moisture powder) As for the graft-ized resultant in connection with this invention, neutralizing with a basic compound is desirable, and it can be easily formed into moisture powder by neutralizing. The compound which vaporizes as a basic compound at the time of paint film formation or printing hardening by curing agent combination is desirable, and ammonia, organic amines, etc. are suitable. As an example of a desirable compound, triethylamine, N,N-diethylethanolamine, N,N-dimethylethanolamine, amino ethanolamine, N-methyl - N, N - Diethanolamine, Isopropylamine, iminobis propylamine, ethylamine, diethylamine, 3-ethoxypropylamine, 3-diethylaminopropylamine, A sec-butylamine, propylamine, methylamino propylamine, Dimethylamino propylamine, methyliminobispropylamine, 3-methoxypropylamine, monoethanolamine, diethanolamine, triethanolamine, etc. can be mentioned. As for a basic compound, it is desirable to use it by partial neutralization or full neutralization, at least, according to the carboxyl group content contained in a graft-ized resultant, so that the range of PH value of a water dispersing element may be 5.0-9.0. If it is the case where the boiling point uses a basic compound 100 degrees C or less, there are also few residual basicity compounds in the paint film after desiccation, and an adhesive property with a metal or the inorganic vacuum evaporatio film, the water resisting property of this layered product, and a heat-resistant water adhesive property are excellent.

[0031] the drainage system dispersing element generated by this invention -- the weight average molecular weight of the polymerization object of a radical polymerization nature monomer -- 500-50000 it is -- a thing is desirable. It is the weight average molecular weight of the polymerization object of a radical polymerization nature monomer 500 Generally it is difficult to control below, graft efficiency falls, and there is an inclination for grant of the hydrophilic radical to copolymerized polyester not to fully be performed. Moreover, although the graft polymerization object of a radical polymerization nature monomer forms the hydration sphere of a particulate material, in order to give the hydration sphere of sufficient thickness and to obtain a stable dispersing element, the weight average molecular weight of the graft polymerization object of a radical polymerization nature monomer is 500. It is desirable that it is above. Moreover, the upper limit of the weight average molecular weight of the graft polymerization object of a radical polymerization nature monomer is 50000 at the point of the polymerization nature in solution polymerization. It is desirable. Control of the molecular weight in within the limits of this can be performed by combining a chain transfer agent and polymerization inhibitor suitably the amount of initiators, monomer drop time, polymerization time amount, a reaction

solvent, a monomer presentation, or if needed.

[0032] In this invention, the reactant which carried out the graft polymerization of the radical polymerization nature monomer to hydrophobic copolymerized polyester resin has self-cross-linking. Dehydration of the silanol group which exists in 1 reactant with the heat at the time of desiccation although a bridge is not constructed in ordinary temperature Intermolecular reactions, such as a hydrogen abstraction reaction by 2 heat radical, are performed, and a bridge is constructed without a cross linking agent. Thereby, the adhesive property and water resisting property which are the purpose of this invention can be discovered for the first time. About the cross-linking of a paint film, although various approaches can estimate, it can investigate at the rate of insoluble matter in the chloroform solvent which dissolves both hydrophobic copolymerized polyester resin and a radical polymerization object. The rate of insoluble matter of the paint film which dries below 80 degrees C, heat-treats for 5 minutes and is obtained at 120 degrees C is 70% or more more preferably 50% or more. When the rate of insoluble matter of a paint film is less than 50%, an adhesive property and a water resisting property are not not only enough, but it will cause blocking.

[0033] Although the above-mentioned graft copolymer remains as it is and can form the adhesion reforming layer which can be used for this invention, it can give an advanced water resisting property to an adhesion reforming layer by hardening by blending a cross linking agent (resin for hardening) further.

[0034] Amino resin; polyfunctional epoxy compound; polyfunctional isocyanate compound; block isocyanate compound; polyfunctional aziridine compounds, such as an alkyl ether compound with which the addition product of a phenol-formaldehyde-resin; urea, a melamine, benzoguanamine, etc. and formaldehyde, and this addition product and a carbon atomic number of a condensate with formaldehyde, such as alkylation phenols and cresol, consist of alcohol of 1-6 as a cross linking agent; an oxazoline compound etc. can be used.

[0035] as phenol formaldehyde resin -- alkylation (methyl --) Ethyl, propyl, isopropyl or a butyl phenol, p-tert-p tert amylphenol, A 4 and 4'-sec-butylidene phenol, p-tert-butylphenol, An o-, m-, p-cresol, p-cyclohexyl phenol, 4, and 4'-isopropylidene phenol, The condensate of phenols, such as p-nonyl phenol, p-octyl phenol, 3-pentadecyl phenol, a phenol, phenyl o-cresol, p-phenylphenol, and a xyleneol, and formaldehyde can be mentioned.

[0036] As amino resin, although the methoxy-ized methylolurea and methoxy-ized methylol N, N-ethylene urea, a methoxy-ized methylol dicyandiamide, a methoxy-ized methylol melamine, methoxy-ized methylol benzoguanamine, a butoxy-ized methylol melamine, butoxy-ized methylol benzoguanamine, etc. are mentioned, a methoxy-ized methylol melamine, a butoxy-ized methylol melamine, methylol-ized benzoguanamine, etc. can be mentioned preferably, for example.

[0037] As a polyfunctional epoxy compound, for example Diglycidyl ether and its oligomer of bisphenol A, Diglycidyl ether and its oligomer of hydrogenation bisphenol A, Orthochromatic phthalic-acid diglycidyl ester, isophthalic acid diglycidyl ester, Terephthalic-acid diglycidyl ester, p-oxy-benzoic-acid diglycidyl ester, Tetrahydro phthalic-acid diglycidyl ester, hexa hydro phthalic-acid diglycidyl ester, Succinic-acid diglycidyl ester, adipic-acid diglycidyl ester, Sebacic-acid diglycidyl ester, ethylene glycol diglycidyl ether, Propylene glycol diglycidyl ether, 1,4-butanediol diglycidyl ether, 1 and 6-hexanediol diglycidyl ether and polyalkylene glycol diglycidyl ether Trimellitic acid triglycidyl ester, triglycidyl isocyanurate, 1, 4-diglycidyl oxybenzene, a diglycidyl propylene urea, Glycerol triglycidyl ether, trimethylolpropane triglycidyl ether, pentaerythritol triglycidyl ether, the triglycidyl ether of a glycerol alkylene oxide addition product, etc. can be mentioned.

[0038] As a polyfunctional isocyanate compound, the diisocyanate of the aromatic series of low-molecular or a giant molecule and aliphatic series and the poly isocyanate more than trivalent can be used. As poly isocyanate, there is a trimer of tetramethylene di-isocyanate, hexamethylene di-isocyanate, toluene diisocyanate, diphenylmethane diisocyanate, hydrogenation diphenylmethane diisocyanate, xylylene diisocyanate, hydrogenation xylylene diisocyanate, isophorone diisocyanate, and these isocyanate compounds. Furthermore, the end isocyanate radical content compound which macromolecule active hydrogen compounds, such as low-molecular active hydrogen compounds, such

as the excessive amount of these isocyanate compounds, ethylene glycol and propylene glycol, trimethylol propane, a glycerol, a sorbitol, ethylenediamine, monoethanolamine, diethanolamine, and triethanolamine, or polyester polyols, polyether polyols, and polyamides, are made to react, and is obtained can be mentioned.

[0039] Conventionally, from a well-known proper approach, blocking isocyanate carries out the addition reaction of the above-mentioned isocyanate compound and the blocking agent, and can prepare them. As an isocyanate blocking agent, for example A phenol, cresol, Phenols, such as a xylenol, resorcinol, a nitrophenol, and chlorophenol; A thiophenol, Thiophenols, such as a methylthio phenol; Acetoxime, methyl ECHIKE talkie SIMM, Oximes, such as a cyclohexanone oxime; A methanol, ethanol, Alcohols, such as propanol and a butanol; Ethylene chlorohydrine, Halogenation alcohols; t-butanols, such as 1 and 3-dichloro-2-propanol, Tertiary alcohol, such as t-pentanol; Epsilon caprolactam, Lactams; aromatic amine; imide, such as delta-valerolactam, nu-butyrolactam, and beta-propyl lactam; An acetylacetone, Activity methylene compound; mercaptans; imines; ureas; diaryl compounds, such as acetoacetic ester and ethyl-malonate ester; sodium bisulfite etc. can be mentioned.

[0040] these cross linking agents are independent respectively -- or two or more sorts are mixed and it can use. As loadings of a cross linking agent, 5 weight sections - 40 weight section is desirable to the graft-ized copolymer 100 weight section. When the approach of dissolving or distributing as the combination approach of a cross linking agent in the drainage system solvent solution of a direct graft copolymer or dispersion liquid when (1) cross linking agent is water solubility, or (2) cross linking agents are oil solubility, there is the approach of adding to reaction mixture after graft-ized reaction termination. These approaches can be suitably chosen according to the class of cross linking agent, and description. Furthermore to a cross linking agent, a curing agent or an accelerator can be used together.

[0041] Although it remains as it is and can form the adhesion reforming layer which can be used for this invention, the above-mentioned graft copolymer mixes conductive resin, such as general-purpose polyester system resin, urethane system resin, acrylic resin, those copolymers, various water soluble resin, etc. various engineering plastics, for example, the poly aniline, and polypyrrole, antibacterial resin, ultraviolet absorption nature resin, and gas barrier nature resin from other purposes, it forms an adhesion reforming layer, and it is peach furnace *****.

[0042] An adhesion reforming layer can be made to contain additives, such as various surfactants, an antistatic agent, inorganic lubricant, organic lubricant, and an ultraviolet ray absorbent, in the range which does not spoil the effectiveness of this invention further.

[0043]

[Example] Hereafter, this invention is explained using an example. It shows weight % that that it is only with the section expresses the weight section, and there is among an example with %. Each parameter followed the following approaches.

(1) Film haze JIS-K6714 It applies correspondingly and is the POIKKU integrating-sphere type HTR by Japan precision optical incorporated company. Meter SEP-H2D The surface haze was searched for according to the form.

(2) What carried out the adhesive evaluation lamination was exfoliated 90 water attachments using the "tensilon UTM 2" by TOYO SOKKI CO., LTD., and it measured and asked for the S-S curve between an adhesion reforming layer and substratum material.

[0044] The copolymerized polyester resin (A-1) 75 section, the methyl-ethyl-ketone 56 section, and the isopropyl alcohol 19 section were put into the reactor equipped with example 1 agitator, a thermometer, reflux equipment, and quantum dropping equipment, it heated and agitated at 65 degrees C, and resin was dissolved. After resin dissolved completely, the maleic-anhydride 15 section was added in the polyester solution. Subsequently, the solution which dissolved the styrene 10 section and the azobis dimethylvaleronitrile 1.5 section in the methyl ethyl ketone of the 12 sections was dropped into the polyester solution by 0.1 ml/min, and churning was continued for further 2 hours. After performing the sampling for analysis from a reaction solution, the methanol 5 section was added. Subsequently, the water 300 section and the triethylamine 15 section were added to the reaction solution, and were agitated for 1 hour. Then, the reactor internal temperature was raised to 100 degrees C, a methyl ethyl ketone,

isopropyl alcohol, and superfluous ammonia were distilled off by distillation, and moisture powder graft polymerization resin (B-1) was obtained. This moisture powder graft resin (B-1) was light yellow transparency.

[0045] This moisture powder graft resin (B-1) was diluted with water:isopropyl alcohol =9:1 (weight ratio) so that it might become 10% of solid content concentration, and coating liquid was adjusted. It is syndiotactic polystyrene (weight average molecular weight 300000) 100 considering a bridge formation polystyrene particle as lubricant. As opposed to weight % The polymer chip added 3.0% of the weight, It is syndiotactic polystyrene (weight average molecular weight 300000) 100 considering a bridge formation polystyrene particle as lubricant. As opposed to weight % It dries, after mixing the polymer chip added 2.0% of the weight and the polymer chip with which lubricant is not added at a rate of 1 to 1 to 8 by the weight ratio. it fuses at 295 degree C -- it extruded from the T die of the lip gap of 200 micrometer, adhesion / cooling solidification was carried out by the electrostatic **** method at the 40-degree C cooling roller, and the 55-micrometer amorphism sheet was obtained.

[0046] The preheating of this amorphism sheet is first carried out to 98 degrees C with a roll, and it is skin temperature. A 750-degree C infrared-heating heater is used and also heated four. film temperature 140 degrees C -- lengthwise direction 3.3 times -- extending -- further -- a 120-degree C roll -- lengthwise direction It extends 1.2 times. Occasion Vertical relaxation processing is performed 12% between a 150 degrees C ceramic roll and a 40-degree C metal roll, subsequently the aforementioned coating liquid is applied by the die coating-machine method, and it dries by 70-degree C hot blast. Further by the tenter film 110 degrees C -- a preheating -- carrying out -- a longitudinal direction -- extension temperature 120 degrees C it extends 3.5 times -- heat setting was carried out for 10 seconds at 265 degree C. then, 230 degree C -- 5% horizontal relaxation processing -- carrying out -- further -- Vertical relaxation processing was carried out 3% between the 220 degrees C ceramic roll and the 40-degree C metal roll. The thickness of the obtained film obtained the 4-micrometer biaxial-stretching syndiotactic polystyrene film. the final amount of coat agent application -- 0.1 g/m2 it was . The evaluation result of this obtained syndiotactic polystyrene film was shown in Table 2.

[0047] Moisture powder graft resin (B-2) was obtained like the example 1 except having changed into the example 2 maleic-anhydride 8 section and the styrene 17 section. This moisture powder graft resin (B-2) was light yellow transparency. The laminating syndiotactic polystyrene film which carried out the laminating of this moisture powder graft resin (B-2) like the example 1 was obtained. The evaluation result of this obtained syndiotactic polystyrene film was shown in Table 2.

[0048] (A-2) was used instead of example 3 copolymerized-polyester resin (A-1), and moisture powder graft resin (B-4) was obtained like the example 1. This moisture powder graft resin (B-4) was light yellow transparency. The laminating syndiotactic polystyrene film which carried out the laminating of this moisture powder graft resin (B-2) like the example 1 was obtained. The evaluation result of this obtained syndiotactic polystyrene film was shown in Table 2.

[0049] The evaluation result of the syndiotactic polystyrene film obtained by the completely same approach as an example 1 was shown in Table 2 except not having an example of comparison 1 adhesion reforming layer.

[0050] The copolymerized polyester resin (A-1) 75 section, the methyl-ethyl-ketone 56 section, and the isopropyl alcohol 19 section were put into the reactor equipped with example of comparison 2 agitator, a thermometer, reflux equipment, and quantum dropping equipment, it heated and agitated at 65 degrees C, and resin was dissolved. After resin dissolved completely, the mixture of the methacrylic-acid 17.5 section and the ethyl-acrylate 7.5 section and the solution which dissolved the azobis dimethylvaleronitrile 1.2 section in the methyl ethyl ketone of the 25 sections were dropped into the polyester solution by 0.2 ml/min, and churning was continued for further 2 hours. After performing the sampling for analysis from a reaction solution, the water 300 section and the triethylamine 25 section were added to the reaction solution, and were agitated for 1 hour. Then, the reactor internal temperature was raised to 100 degrees C, a methyl ethyl ketone, isopropyl alcohol, and superfluous triethylamine were distilled off by distillation, and moisture powder graft resin (B-5) was obtained. The obtained resin (B-5) was light yellow transparency. The laminating syndiotactic polystyrene film which carried out the

laminating of the above-mentioned moisture powder graft resin by the same approach as an example 1 was obtained. The evaluation result of this obtained syndiotactic polystyrene film was shown in Table 2.

[0051]

[Effect of the Invention] As mentioned above, as a publication, when this invention adopts the configuration as a publication as said claim, the laminating syndiotactic polystyrene system biaxially oriented film excellent in transparency and an adhesive property is offered.

[0052]

[Table 1]

| 共重合組成(モル%) | A-1 |
|--------------|-------|
| テレフタル酸 | 70 |
| セバシン酸 | 26 |
| フマル酸 | 4 |
| エチレングリコール | 50 |
| 1, 4-ブタンジオール | 50 |
| 重量平均分子量 | 20000 |

[0053]

[Table 2]

| | ヘイズ (%) | 接着強度 (g/15mm) | 総合評価 |
|------|------------|------------------|------|
| 実施例1 | 4.5 | 180 | ◎ |
| 実施例2 | 4.6 | 170 | ◎ |
| 実施例3 | 4.5 | 150 | ○ |
| 比較例1 | 4.1 | 20 | △ |
| 比較例2 | 6.2 | 50 | × |

[Translation done.]

* NOTICES *

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The easy adhesiveness syndiotactic polystyrene system film which is the self-cross-linking polyester system graft copolymer with which the graft of one or more sorts of polymerization nature partial saturation monomers was carried out to hydrophobic polyester resin at least at one side of the film which consists of the styrene system polymer which has syndiotactic structure substantially, and carried out the laminating of the adhesion reforming layer characterized by including at least one sort of monomers in which said graft copolymer contains the acid anhydride which has a double bond.

[Claim 2] The easy adhesiveness syndiotactic polystyrene system film according to claim 1 formed when the layer which makes a constituent said self-cross-linking polyester system graft copolymer carried out heat setting after spreading and desiccation and of this film for the coating liquid containing a self-cross-linking polyester system graft copolymer to un-extending or an uniaxial stretched film after extension one shaft or more than it further.

[Claim 3] Claim 1 characterized by said polymerization nature partial saturation monomer containing the anhydride and styrene of a maleic acid at least, an easy adhesiveness syndiotactic polystyrene system film given in either of two.

[Translation done.]